National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 1879a

Respirable Cristobalite
(Quantitative X-Ray Powder Diffraction Standard)

This Standard Reference Material (SRM) is intended for use in preparation of calibration standards for quantitative analyses of cristobalite by x-ray powder diffraction in accordance to National Institute for Occupational Safety and Health (NIOSH) Analytical Method 7500 [1] (or equivalent). A unit of SRM 1879a consists of approximately 5 g of powder bottled under argon.

Material Description: The SRM material was prepared from high purity fused quartz powder which was annealed at 1600 °C for 2 h. This operation was done in a furnace which allowed for insertion of the SRM material at operating temperature and under a controlled atmosphere. The resulting high porosity sintered form was crushed and jet milled to a median particle size of 3.5 µm. The powder was washed in hydrofluoric acid and hydrochloric acid, rinsed, ignited at 500 °C, and bottled.

An analysis of the quantitative results from Rietveld analyses of x-ray powder diffraction data indicated that the SRM material was homogeneous with respect to diffraction properties.

Certified Value and Uncertainty: The certified purity of the material, expressed as a mass fraction in %, is:

95.6 % ± 0.4 % crystalline cristobalite

The interval defined by the certified value and its uncertainty is expressed as a 95 % confidence interval in the absence of systematic error [2].

Expiration of Certification: The certification of this SRM is deemed to be indefinite within the stated uncertainties, provided the SRM is stored and handled in accordance with the Storage section of this certificate. This material degrades with exposure to humidity. If excessive exposure is suspected, discontinue use.

This SRM was prepared and certified by J.P. Cline of the NIST Ceramics Division and R.B. Von Dreele of Manuel Lujan, Jr., Neutron Scattering Center (LANSCE), Los Alamos National Laboratory. The annealing operation was performed by Pyromatics Corp., Willoughby, OH, under the supervision of J. Blackmer.

Statistical analysis was performed by J.J. Filliben of the NIST High Performance Systems and Services Division.

The technical and support aspects involved in the preparation, certification, and issuance of this SRM were coordinated through the NIST Standard Reference Materials Program by R.J. Gettings.

Stephen W. Freiman, Chief
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Gaithersburg, MD 20899
Certificate Issue Date: 31 August 1999

Thomas E. Gills, Director
Office of Measurement Services

Certification: The SRM was certified with respect to the mass fraction of material which exhibits Bragg scattering in correspondence to that of cristobalite. The certified value was determined with a Rietveld [3] analysis of neutron time-of-flight (TOF) powder diffraction data. The homogeneity of the SRM material was verified with Rietveld analyses of x-ray powder diffraction (XRD) data. These latter refinements were also used to determine the reported, non-certified, lattice parameters.

The certification method for SRM 1879a utilized SRM 676 Alumina Standard for Quantitative Analysis by X-Ray Powder Diffraction [4] as the internal standard in conjunction with the unbiased neutron TOF diffraction measurements. The studies undertaken in conjunction with the certification of SRM 676 [5,6] included the characterization of its amorphous content. Therefore, SRM 676 is suitable for determining the amorphous content in unknowns. The quantitative results from Rietveld analyses of XRD data displayed a systematic bias of less than 2 %; however, these results were as precise as those determined from the TOF data. It should be noted that the mechanism inducing this bias is not operative in Reference Intensity Ratio (RIR) based methods [7].

The amorphous content of SRM 676 was determined through a comparison of the phase abundance within a series of mixtures consisting of SRM 676 and high purity silicon powder [5]. The silicon was crushed and jet milled from electronic grade Czrochralski grown boules. The resulting powder was fractionated into five lots of varying particle size (surface area) and then annealed. The surface area of each lot was measured via Brunauer-Emmett-Teller (BET) adsorption. Mixtures of 50 % silicon, from each lot, and 50 % alumina from SRM 676 were prepared. Implicit in the interpretation of the data was the assumption that all amorphous material associated with the silicon is confined to the crystallite surface and the amorphous layer thickness is invariant with respect to crystallite size. Thus, the amorphous content of the silicon could be systematically varied by altering its surface area. A Rietveld analysis of neutron TOF data collected on the mixtures yielded the mass fraction of crystalline silicon. These data were plotted relative to the surface area, or amorphous content, of the silicon of each sample. An extrapolation of these data yielded the mass fraction of silicon from a hypothetical sample from which it would possess “zero” amorphous content. Thus, the discrepancy between this mass fraction and that of the initial weighing would indicate the true amorphous content of the alumina. Analysis of the TOF data yielded credible crystallographic structure parameters for both the silicon and alumina, a silicon oxide layer thickness of 3.0 nm, which is consistent with accepted values, and an amorphous content associated with SRM 676 of 1.58 %.

Five randomly selected samples from the SRM 1879a material were admixed with SRM 676 at the 50 % level for TOF neutron diffraction analysis. TOF data were obtained on the High Intensity Powder Diffractometer (HIPD) at the LANSCE. The samples were contained in 9.5 mm diameter by 50 mm long vanadium cans during the analysis. Each sample was exposed to the neutron beam for 1.3 h with the LANSCE source operating at 70 µA proton beam current. Data used for this certification were obtained from detector banks positioned at ± 90° and ± 153° 2θ. The ± 90° banks covered a d-spacing range of 0.05 nm to 0.63 nm, while the ± 153° banks covered 0.05 nm to 0.48 nm. Rietveld refinements using the General Structure Analysis System (GSAS) [8] of the phases in these samples included: scale factors, lattice parameters, atomic positional and thermal parameters, crystallite size and microstrain [9] parameters, an absorption factor, and six terms of a background function describing the effects of thermal diffuse and incoherent scattering for each data set. The amorphous phase content was determined from the discrepancy between the measured silicon oxide to alumina ratio and that calculated presuming the material was 100 % crystalline.

X-ray diffraction data for homogeneity testing and lattice parameter determination were collected on two specimens removed from each of ten randomly selected bottles of the SRM material; these 10 bottles included those from which the TOF specimens were prepared. These specimens also had known amounts of SRM 676 admixed with them. These XRD data were collected on a Siemens D500[1] diffractometer equipped with a focusing Ge incident beam monochromator, sample spinner, and a scanning position sensitive detector. Copper $K\alpha_1$ radiation $\lambda = 0.15405945$ nm [10] was used. The scan range was from 18° to 154° 2θ. GSAS was used for a Rietveld refinement of the two phases as outlined in Reference 11. Refined parameters included: scale factors, crystallite size and strain induced

[1] Certain commercial materials and equipment are identified in order to adequately specify the experimental procedure. Such identification does not imply a recommendation or endorsement by NIST, nor does it imply that the materials or equipment are necessarily the best available for the purpose.

broadening terms of the pseudo-Voigt profile function [12], one of the two parameters of the Finger [13] model for profile asymmetry, lattice parameters, sample shift and transparency terms, atomic thermal and position parameters, and five terms of a background function describing the effects of thermal diffuse scattering and air scattering (incoherent) of the incident beam. Gaussian U, V, and W terms [14] were presumed to be instrumental in origin and fixed at those obtained from a refinement of SRM 660, the $\mathrm{La6_6}$ line profile standard [15].

Storage: SRM 1879a was bottled under argon to protect against humidity. When not in use, store the unused portion of this powder tightly capped in the original bottle or in a manner with similar or greater protection against humidity.

Information Values and Uncertainties: The information values for lattice parameters as determined by the Rietveld method and particle size distribution as determined by laser scattering are given in Table 1 and Figure 1, respectively. The interval defined by a value and its uncertainty is a 95 % confidence interval for the true value of the mean in the absence of systematic error.

A very small, diffuse peak located at ~21° 2θ is consistent with a trace amount of a tridymite phase.

Table 1. Lattice Parameters as Determined by the Rietveld Method

	Lattice Parameter (nm)
a	0.4972125 ± 0.0000038
c	0.6925906 ± 0.0000055

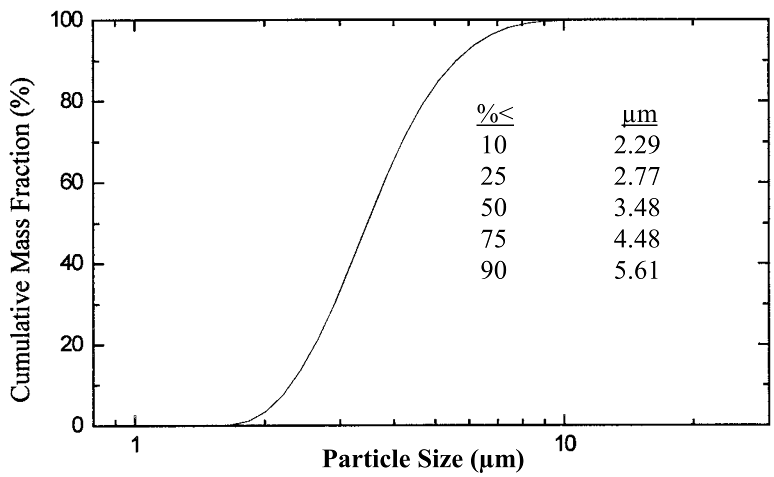

Figure 1. Typical Particle Size Distribution by Laser Scattering

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